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(21) International Application Number: PCT/EP98/03983 (22) International Filing Date: 30 June 1998 (30.06.98) (30) Priority Data: RM97A000391 1 July 1997 (01.07.97) IT (71) Applicant (for all designated States except US): KEMPRO ITALIANA S.R.L. [IT/IT]; Via Cancelleria, 45, I-00040 Ariccia (IT). (72) Inventor; and (75) Inventor/Applicant (for US only): TODARELLO, Francesco [IT/IT]; Via del Fosso dell'Acqua Mariana, 94, I-00040 Ciampino (IT). (74) Agent: GERVASI, Gemma; Notarbartolo & Gervasi S.p.A., Corso di Porta Vittoria, 9, I-20122 Milan (IT).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the</i> <i>claims and to be republished in the event of the receipt of</i> <i>amendments.</i>
(54) Title: PROCESS TO OBTAIN A HIGH-CONCENTRATION COLLOIDAL SILICA SUSPENSION AND PRODUCT THUS OBTAINED		
(57) Abstract Process to obtain a colloidal silica suspension in a concentration above the corresponding gel point, wherein the basic silica suspension resulting from concentration at boiling is subjected to ultrafiltration substantially at room temperature or below, the low-temperature step being carried out as rapidly as possible.		

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PROCESS TO OBTAIN A HIGH-CONCENTRATION COLLOIDAL SILICA SUSPENSION AND PRODUCT THUS OBTAINED

Field of the invention

The present invention refers to a process to obtain a colloidal silica suspension in a high concentration, in particular in a concentration above the corresponding gel point. The invention also refers to the product thus obtained.

Prior art

Suspensions based on SiO_2 , containing silica with dimensions in the order of nanometres and having alkaline pH, also called basic sol, and acid suspensions, called acid sol, are already known and find application, e.g., as bonding agents to be used at high temperatures in precision casting.

Suspensions of this type, obtained by conventional methods, are described in GB patent 1,348,705. The production process disclosed therein is based on an ultrafiltration step to be accurately monitored, especially with regard to the salts content, to prevent the occurrence of irreversible gel formation.

US patent 5,458,812 describes a process to obtain colloidal silica based on the use of three reactors in series. In this case too, the final suspension is concentrated by ultrafiltration.

Both aforementioned methods allow to produce colloidal silica suspensions with dispersed particles size in the order of some tens of nanometres. In fact, in said processes, at a given average size of the water-dispersed silica particles, there is a limit concentration value, called gel point, below which gelling phenomena take place spontaneously with aggregation of the silica particles. Said well known values (R.K. Iler, The Chemistry of Silica, John Wiley & Sons, NY), provide evidence that the smaller the particle size, the lower is the concentration at which the particles gel spontaneously. The values, at a pH of approx. 9.5, are reported below:

<u>Average particle size</u>	<u>Gel point</u>	<u>Specific surface</u>
(nm)	(% by wt.)	m ² /g
5	8-20	550
7	33-36	392
12	45-50	229
22	55-60	125

Said particle size generally corresponds to the indicated specific surface ranges, obtained by applying the following formula:

$$\text{Specific Surface (m}^2\text{/g)} = 2750 / \text{particle diameter (nm)}$$

(reference number)

Therefore, having set the particle size, it is impossible to obtain concentrations above the corresponding gel point.

Specific operational conditions overcoming the deficiencies of the prior art have now been found.

Summary

It is, therefore, an object of the present invention to provide a process to obtain a sol based on colloidal silica in a concentration above the corresponding gel point.

Another object of the invention resides in an alkaline suspension based on colloidal silica having a silica content above the corresponding gel point.

A further object of the invention resides in the use of alkaline suspensions based on colloidal silica, having a silica content above the corresponding gel point, as bonding agents in precision casting.

Still further objects of the invention will become evident from the detailed description of the invention.

Detailed description of the invention

Unless otherwise specified, in the present description, all % are expressed as % by weight.

The stable starting suspension, which may be used in the process according to the invention, is obtained by causing an aqueous solution of an alkaline metal silicate, e.g. sodium silicate in an SiO₂/Na₂O ratio equal to approx. 3.36:1 (solution containing approx. 5-6% by wt. SiO₂), to pass, at room temperature, through a

strong cationic ion exchange column, e.g. RELITE® CF available from Resindion, to give unstable silicic acid (acid sol) at a final pH of 2 to 3.5.

Acid sol is stabilized at room temperature as follows. The solution is vigorously stirred and rapidly added with an alkaline silicate, abruptly to bring the pH value, initially of approx. 2, to a final value of 9 to 11.

For example, approx. 10 m³ of acid sol may be added with approx. 800 l of a 20-30% by wt. sodium silicate solution, to bring alkalinity of the former acid sol to approx. 140-160 meq/l alkalinity.

Purpose of such a rapid alkalis addition is to leave the critical pH zone as rapidly as possible, where spontaneous gel formation phenomena tend to occur.

The stabilized suspension is fed to appropriate evaporators and heated. Said concentration is carried out at boiling, at a temperature ranging from about 90° to about 98°C, preferably of approx. 95°C, under vacuum, until obtaining a final concentration SiO₂ of approx. 5-15% by wt., preferably of approx. 6% by wt., a pH ranging between 9 and 10 and particle size below 10 nm., preferably in the range of 2 to 5 nm.

When the desired concentration is obtained, the suspension is subjected to cold ultrafiltration by causing said suspension to cool from the boiling temperature to room temperature as rapidly as possible, e.g. by appropriate heat exchangers. To get an idea of the time taken for said operation of cooling, note that the temperature decreases to 15-30°C within a couple of hours.

For ultrafiltration, membranes known to those expert in the art, e.g. flat or spiral membranes with a cut of 10,000 to 30,000 dalton, may be conveniently used.

Since the suspension tends to heat when passing through the membrane, it is advisable to control the temperature, which shall not exceed 50°C, otherwise the cut will change, i.e. increase.

By carrying out the ultrafiltration as described in the above, the starting suspension will concentrate, while the starting particles diameter will be maintained: (2-5 nm, with specific surface of 500-1000 m²/g). It follows that, once ultrafiltration has been completed, a suspension with silica particles size below 10 nm and with a concentration higher than 50% by wt., preferably higher than 30% by wt., is obtained.

Downstream of ultrafiltration, it is necessary to adjust the content of cations and anions, which have been concentrated by passing through the ultrafiltration membranes. Said ion adjustment step is of some importance; in fact, should it not be adequately performed, it will cause suspension instability and gelling.

Said adjustment may be carried out by techniques known to those expert in the art, e.g. using ion exchange resins.

Within the scope of the present invention, said adjustment is conveniently carried out as follows. An amount of product, preferably 20 to 50% of the total, is caused to pass through a bed of strong cationic resin, e.g. RELITE® CF available from Resindion, which captures sodium. The resulting acid sol is mixed with the remainder of the product. An amount, preferably from 20 to 50% of the total, is withdrawn from the resulting mixture and caused to pass through a bed of weak anionic resin, e.g. RELITE® 4MS available from Resindion. The eluate is mixed with the remainder of the product.

Preferably, the final concentrations of stabilizing ions, compatible with the silica particle size and the concentrations obtained according to the invention, are as follows:

sulphate ions: 20 to 400 mg/l, preferably 100 to 170 mg/l

sodium ions: 0.10 to 0.80% by wt., preferably 0.27 to 0.40% by wt. for a specific surface of 400 to 600 m²/g, preferably 527 to 550 m²/g.

The concentrated solutions of the invention - because of their higher degree of concentration - find more extensive application than the corresponding, less concentrated, solutions. As known, in fact, colloidal silica may be used as a flocculating agent, e.g. in the food industry instead of bentonite, or as an additive for plastic materials and for paper manufacture.

The suspensions of the invention, because of their higher degree of concentration, are particularly effective for white wine and fruit-juice clarification and increase the yield to clarified product.

In the field of plastics for food, the suspensions of the invention, thanks to their wider specific surface, are of great interest being osmoregulators more effective than the products already known.

As concerns paper manufacture, the suspensions of the invention are particularly advantageous as they provide liquid retention.

In particular, the concentrated solutions according to the invention may be advantageously applied to investment casting techniques as low-environmental-impact water-based bonding agents.

The following examples are to be considered illustrative, and not limitative of the scope of the present invention.

Example 1

Description of colloidal silica production process

Vitreous silicate ($\text{SiO}_2/\text{Na}_2\text{O}$ ratio equal to 3.36) was fed to an autoclave at a pressure of 5 to 6 atm with an amount of H_2O adequate to obtain a final silicate concentration of 25% by weight. Said solution, which was turbid because of the presence of clay derived from siliceous sands, was predecanted and then fed to a flocculating tank wherein it was further diluted with water to approx. 20%. The solution was then heated under stirring to a temperature of approx. 70°C , added with low-molecular-weight cationic flocculants, allowed to stir at said temperature for approx. 2 h, and decanted for 48 h. The clarified liquid recovered was further diluted with water to approx. 5%. The resulting diluted solution was caused to pass through a column containing strong cationic resin RELITE® CF to exchange the silicate sodium with the resin hydrogen ion to give unstable colloidal silicic acid (acid sol). An amount of 10 m^3 of said acid sol was fed to a tank provided with a stirrer, marine screw propeller type, and stirred vigorously. Alkaline silicate (800 l) was added rapidly to bring the pH value from 2 to approx. 10. The stabilized solution was heated to boiling (95°C) under vacuum until a final SiO_2 concentration of approx. 6% by wt. with pH of approx. 9.5 and particle size of 2 to 5 nm. The suspension was cooled from 95°C to room temperature over a couple of hours and subjected to ultrafiltration. Ultrafiltration was carried out with a flat membrane with a cut of 20,000 dalton. Once ultrafiltration had been completed, a suspension with silica particles averagely sized 2.6 nm was obtained.

Downstream of ultrafiltration, the content of cations and anions was adjusted by withdrawing an amount of product equal to 30% of the total, and causing it to pass through a bed of strong cationic resin, RELITE® CF, which captures sodium. The

resulting acid sol was mixed with the remainder of the product. An amount equal to 30% of the total was withdrawn from the resulting mixture and caused to pass through a bed of weak anionic resin, RELITE® 4MS. The eluate was mixed with the remainder of the product.

The final product obtained exhibited the following characteristics:

concentration 25% by wt. silica;

surface area 530 m²/g;

particle diameter 2.6 nm.

The product obtained, hereinafter referred to as K, was taken as sample for the successive tests.

Example 2

Stability test. An amount of sample K, having initial temperature of 20°C, density of 1.14 g/cc, viscosity of 11 sec (Ford cup B4) and pH 10, was maintained at 60°C for 20 days. After said period, equivalent to 200 days at room temperature, the product, at 60°C, had density of 1.13 g/cc, viscosity of 11 sec (Ford cup B4) and pH 10. After 20 further days at 60°C, no significant variation took place, which proved a very high stability.

Example 3

Manufacture and characterization of ceramic shells for precision castings

Tests were carried out with sample K and with a non-ultrafiltered comparison sample having the following characteristics: density 1.2 kg/dm³, SiO₂ 30% by wt., pH 9.5, Na₂O 0.30%, particle diameter 12 nm, specific surface 300 m²/g, Cl⁻ 50 ppm, SO₄²⁻ 450 ppm, hereinafter referred to as A.

The comparison sample was selected on the basis of the following criterion: the product had to show a specific surface smaller than that of reference, which was of 500 m²/g min., and a higher silica content. In this way, the effect of said two physical data on the mechanical resistance and permeability could be investigated.

The goal was to demonstrate how a reduced silica content (with consequent reduction in the overall product cost), compensated by an increased specific surface, could maintain the mechanical properties (breaking modulus MOR at

room temperature and at high temperature) at industrially acceptable standards and increase the permeability properties at room and at high temperature (900°C). Shells were produced according to the following procedure:

- Making wax components by means of a press injecting synthetic material in the liquid state under pressure into a mould.
- Assembling the wax components by welding, to obtain units (clusters) inclusive of the components to be produced, of gates, ceramic connection areas, if any, to be coated with refractory material.
- Coating the clusters with ceramic material through a small number of alternate immersions into baths containing bonding agents and ceramic material and sprinklings with refractory sand.

Said operations allowed the obtainment of a ceramic shell, which was subjected to final drying under controlled humidity and temperature conditions.

- Removing the wax from the ceramic shell by dewaxing in an autoclave at a pressure of 10 atm max.

The shells obtained were called shells K and shells A.

For the purpose of comparison, baths for the manufacture of ceramic shells usable for casting, were prepared with both samples, K and A. The manufacturing cycles varied depending on the intermediate drying times and on the relative conditions (with or without ventilation) according to Table 1.

Table 1

	<u>Bonding agent A</u>	<u>Bonding agent K</u>
1 h intermediate drying without ventilation	A1	K1
1 h intermediate drying with ventilation	A1V	K1V
nh intermediate drying without ventilation	An	Kn
nh intermediate drying with	AnV	KnV

Primary and secondary baths, as per Table 2, were prepared for both bonding agents A and K.

Table 2

Bonding agent	Bonding agents A and K
Primary bath flour	Zircosil - 200 mesh
Primary bath load/ bonding agent ratio	4.5 kg/l
Wetting agent	0.5% SYNPERONIC
Viscosity (primary bath)	90" (FORD B4)
Secondary bath flour	Molochite - 200 mesh
Secondary bath load/ bonding agent ratio	2 kg/l
Viscosity (secondary bath)	30" (FORD B4)

Ceramic shells were prepared with the abovesaid baths according to the procedures shown in Table 3. Baking and casting conditions for shells obtained with bonding agents A and K are reported in Table 4. Mechanical tests were performed on the thus obtained shells, the breaking modulus MOR being determined at room temperature and at 900°C. Tests were carried out with a NEITZSCH TESTER 422S apparatus.

Tabl 3

<u>Sprinkling sand</u>		
No. of primary layers	1	zircon 80/120
No. of secondary layers	3 3 + finishing	molochite 30/80 molochite 30/80
Intermediate drying	1 to 4 h	
Final drying	24 h	
Drying conditions	45%±5% UR 21.5±1.5°C with/without ventilation	
Dewaxing in autoclave	8 atm for 10min	

Table 4

	<u>shell A.</u>	<u>shell K.</u>
Shells cast (identification)	A1(2) and A1V	K1(2) and K1V
Test castings	3	3
Preheating conditions	1150°C 1h	1150°C 1h
Type of alloy	AISI 316	AISI 316
Casting temperature	1550°C	1550°C
Remarks	solid casting	solid casting
Surface quality	good	good

Hot temperature tests were carried out according to the following procedure:

- test-pieces dewaxing in autoclave
- baking up to 1000°C with no temperature pause
- low cooling in oven
- test-piece positioning in the apparatus at room temperature
- test-pieces heating inside the apparatus to 900°C
- flexural test at hot temperature

As concerns the tests carried out at room temperature, the values of the breaking modulus of shells obtained with bonding agent A (with or without forced ventilation) are averagely higher than those obtained with bonding agent K. (Table 5 - Values of breaking modulus at room temperature and at 900°C expressed as MPa)

Table 5

<u>Temperature</u>	<u>room</u>				<u>900°C</u>	
	1	2	3	4	1	4
Intermediate drying time						
A	6.63	6.86	6.56	8.57	14.65	15.20
AV	6.29	7.40	6.21	7.26	14.65	14.35
K	5.12	5.86	6.15	6.77	15.05	14.45
KV	5.60	5.17	5.62	5.68	13.05	14.90
Reference industrial value	5	5	5	5	12	12

In any case, in both cases the values are higher than 5 MPa, which is regarded, by some industrial foundries, as a minimum reference value.

The heat resistance values (after 1 and 4 hrs of intermediate drying) (Table 5) are comparable with the reference ones, however higher than an industrial value of 12 MPa.

It is to be reminded that the breaking modulus is a measure of the stress the test-piece is subjected to; said measure depends considerably on the shell thickness.

However, a measure of the overall resistance of the shell is given by the tensile strength. (see Table 6 - Tensile strength at room temperature expressed as N). As may be seen in Table 6, shells K are averagely more resistant than shells A. The higher resistance, expressed by a higher tensile strength, is strongly correlated with the occurrence of cracks in ceramic shells.

Table 6

<u>Ventilation times and conditions (hrs)</u>	<u>A</u>	<u>K</u>
1	31	25.8
1V	25.4	29
2	31.3	41.7
2V	32.3	28.3
3	32.4	35.7
3V	23.8	28
4	37.5	49
4V	28.3	28.5

Permeability tests at room temperature and at 900°C were conducted on the shells obtained. Tests were carried out according to ICI 775-83 standard.

Permeability tests are usually carried out to predict the behaviour of shells during dewaxing and to know their filling characteristics. A good permeability at room temperature is correlated with good shell performance during dewaxing (absence of cracks); instead, at a high temperature it is indicative of alloy filling inside the ceramic moulds.

The comparison of the tests conducted on samples A and K evidences that, at room temperature, the two products exhibit almost the same characteristics, whereas at a high temperature (900°C), the products of the invention are decidedly better. (see Table 7 - Permeability tests at room temperature and at 900°C).

Tabl 7

<u>Test-piece</u>	<u>Permeability at room T (10^{-5})</u>	<u>Permeability at 900°C (10^{-5})</u>
A3/1	84.9	6.29
A3/2	83.5	6.96
A3/3	92.7	6.55
A3/4	99.3	7.55
A2V/1	103	10.4
A2V/2	96.4	6.82
A2V/3	88.2	6.24
A2V/4	94.6	6.39
A2V/5	103	8.79
K3/1	178	20.6
K3/2	204	28.8
K3/3	188	25.5
K3/4	197	25.5
K3/5	200	29.1
K2V/1	169	28.1
K2V/2	171	24.8
K2V/3	184	26.2
K2V/4	185	26.2
K2V/5	164	20.6

Claims.

1 1. Process to obtain a colloidal silica suspension in a concentration above its gel
2 point consisting in the steps of:

- 3 - preparing a stable suspension by causing an aqueous solution of an alkaline
4 metal silicate to pass, at room temperature, through a strong cationic ion
5 exchange column to obtain unstable silicic acid at a final pH of 2 to 3.5;
- 6 - stabilizing the acid sol at room temperature by vigorous stirring and rapidly
7 adding an alkaline silicate, abruptly to bring the pH final value to 9-11;
- 8 - feeding the stabilized suspension to evaporators and concentrate said
9 suspension at a temperature ranging from approx. 90° to 98°C under vacuum until
10 obtaining a final concentration of SiO₂ of approx. 5 to 15% by wt., the pH ranging
11 from 9 to 10, and the particle size being lower than 10 nm;
- 12 - subjecting the suspension to cold ultrafiltration, wherein said suspension is
13 cooled from boiling temperature to room temperature or below as rapidly as
14 possible.

1 2. The process as claimed in claim 1, wherein the silicate is sodium silicate in an
2 SiO₂/Na₂O ratio equal to approx. 3.36:1.

1 3. The process as claimed in claim 1, wherein, in the ultrafiltration step, cooling is
2 conducted over two hours.

1 4. The process as claimed in claim 1, wherein, in the ultrafiltration step, cooling is
2 conducted until a temperature of 15 to 30°C.

1 5. The process as claimed in claim 1, wherein ultrafiltration is carried out on
2 membranes with a cut of 10,000 to 30,000 dalton.

1 6. The process as claimed in any of claims 1 to 5, wherein, in the ultrafiltration
2 step, the temperature is controlled to maintain it below 50°C.

1 7. The process as claimed in any of claims 1 to 6, wherein the ultrafiltration step
2 is followed by a sol stabilization step, carried out as follows: a suspension amount
3 equal to 20 to 50% of the total, is caused to pass through a bed of strong cationic
4 resin, which captures sodium; the resulting acid sol is mixed with the remainder of
5 the product; then, an amount ranging from 20 to 50% of the total, is withdrawn
6 from the mixture obtained and caused to pass through a bed of weak anionic
7 resin, mixing the eluate with the remainder of the product.

- 1 8. The process as claimed in claim 7, wherein the final concentrations of the
2 stabilizing ions compatible with the particle size and silica concentrations are as
3 follows: sulphate ions: 20 to 400 mg/l, sodium ions: 0.10 to 0.80% by wt., for a
4 specific surface of 480 to 600 m²/g.
- 1 9. The process as claimed in claim 7, wherein the final concentrations of the
2 stabilizing ions compatible with the particle size and silica concentrations obtained
3 according to the invention are as follows: sulphate ions: 100 to 170 mg/l, sodium
4 ions: 0.27 to 0.40% by wt., for a specific surface of 527 to 550 m²/g.
- 1 10. A colloidal silica alkaline suspension having a concentration above its gel point
2 and including silica particles having dimensions lower than 10 nm and a
3 concentration higher than 50% by wt.
- 1 11. A colloidal silica alkaline suspension having a concentration above its gel point
2 and including silica particles having dimensions lower than 10 nm and a
3 concentration higher than 30% by wt.
- 1 12. Use of the suspension as claimed in any of claims 10 and 11 as a flocculant.
- 1 13. Use of the suspension as claimed in any of claims 10 and 11 as a flocculant
2 for food.
- 1 14. Use of the suspension as claimed in any of claims 10 and 11 as an additive for
2 plastics for food.
- 1 15. Use of the suspension as claimed in any of claims 10 and 11 as an additive for
2 paper manufacture.
- 1 16. Use of the suspension as claimed in any of claims 10 and 11 as low-
2 environmental-impact water-based bonding agent for investment casting
3 techniques.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 98/03983

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C01B33/148 C01B33/143 A23L1/059 A23L2/82 C12H1/02
D21H17/68 B22C1/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C01B

Documentation searched other than minimum documentation in the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	EP 0 569 813 A (BAYER AG) 18 November 1993 see the whole document & US 5 458 812 A (BREKAU ET AL.) 17 November 1995 cited in the application ---	11, 16 1-9
X A	GB 1 181 296 A (NALCO CHEMICAL COMPANY) 11 February 1970 see claims 1-5 see page 2, line 19 - line 47 see example 1 --- -/--	11, 16 1

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 98/03983

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2 750 345 A (GUY B. ALEXANDER) 12 June 1956 see the whole document see column 7, line 46 - line 55	11
A	---	1
A	EP 0 537 375 A (NISSAN CHEMICAL IND LTD) 21 April 1993 see claims 1,2,6,7 see column 21, line 16 - line 29	1,2,4, 6-8,10, 11,16
A	---	
A	US 4 915 870 A (JONES ROBERT D) 10 April 1990 see the whole document	1,10,11
A	---	
A	EP 0 464 289 A (NALCO CHEMICAL CO) 8 January 1992 see page 2, line 1-4 see claims 8-10	1,10,11, 15,16
A	---	
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